

FINAL REPORT

ON

THE SYNTHESIS OF MONOMERS WITH PENDENT ETHYNYL GROUP FOR MODIFIED
HIGH PERFORMANCE THERMOPLASTICS

NASA GRANT: NAG - 1 - 905

PROJECT PERIOD: September 1988 to August 31, 1994

by

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MONOMERS WITH PENDENT ETHYNYL
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SUMMARY OF RESULTS AND ACCOMPLISHMENTS

Synthetic schemes were developed and optimized for twelve new monomers possessing unique structural features and one aspartimide. Two synthetic pathways were compared for preparation of the triarylethane monomers with pendent ethynyl groups. The results show that one of these pathways can be generally applied. The alternative pathway was applicable to the preparation of only one of the twelve compounds, the problem being secondary reactions of the initially formed desired product.

This project provided total thesis material and financial support for two master of science(MS) students and partial support for three graduate students. One undergraduate participated for more than a year on the project and received tuition and stipend support for one year.

Three papers were published in refereed journals and five presentations at professional meetings were made based on results related to this project. Two master of science theses also resulted from this work.

A. INTRODUCTION

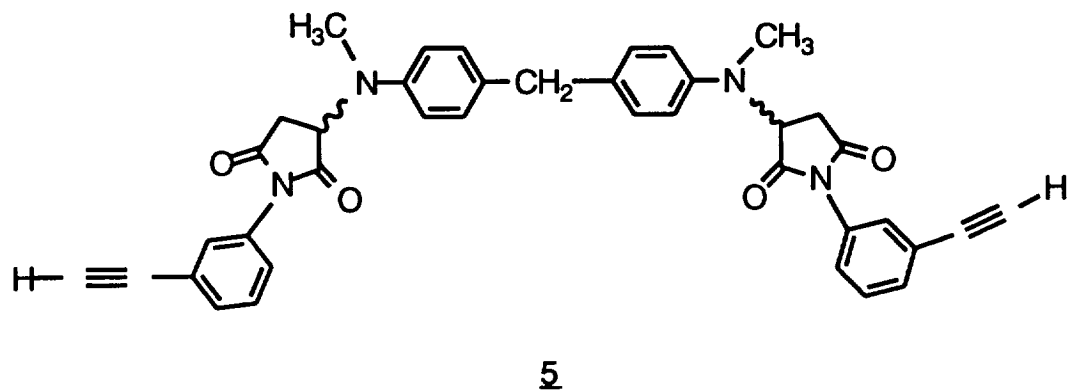
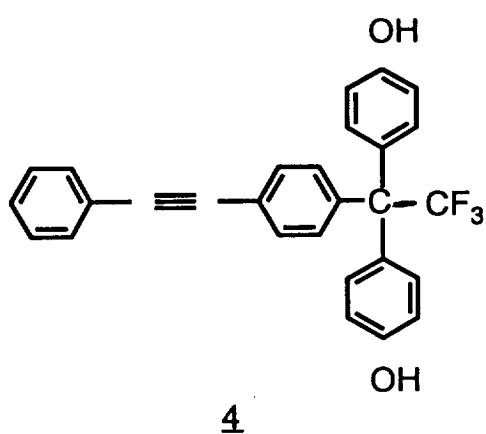
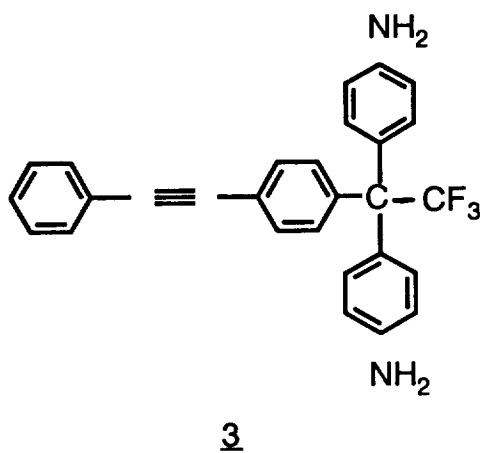
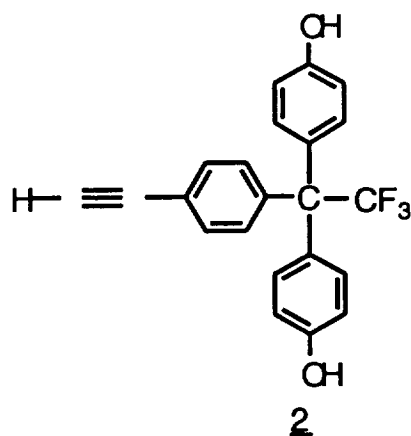
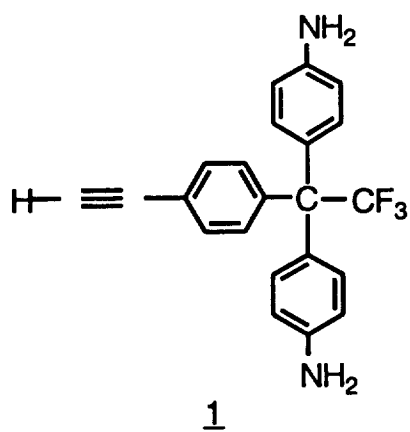
The objectives of this project, which was started in September 1988, were to develop synthetic schemes for the following classes of new monomers: (1) difunctional triarylethanes with pendent acetylenic groups and (2) tertiary aspartimides with terminal acetylene groups at the two ends. Our efforts have resulted in the successful development of high yield schemes for the syntheses of several diamino- and diphenolic analogs of difunctional triarylethanes with pendent ethynyl group (Table I). A scheme for one new tertiary aspartimide has also been established. Multi-gram samples of all prepared new monomers have been provided to our technical contact at NASA-LaRC for polymerization studies. Details of the accomplished work within the grant period is described here. It should be noted that this project has been funded for four out of the six years. We have maintained activity on the project through 1991-92 and 1993-94 under conditions of no-cost extensions. Interim reports were submitted each six months for the first year and a half of this project. Progress reports have been included in all renewal applications.

B. RESULTS AND DISCUSSION

In 1988, we started this project on polymer optimization involving the development of synthetic schemes for difunctional condensation monomers bearing pendent ethynyl groups as the reactive functions for cross-linking of the resulting linear condensation polymers. The initially targeted monomers were the diamino- and

bisphenolic triarylethanes 1 — 4, and the acetylene-capped tertiary aspartimide 5
(Table I).

Table I



B.1. The Synthesis of Bisamino-Analogs of Triarylethanes with Pendent Ethynyl Group.

At the beginning of this project, it was not known whether the acetylenic function on monomers such as 1 — 4 (Table I) would survive the usual condensation polymerization reaction temperature of ~155°C. An early resolution of this uncertainty about the survivability of the ethynyl functional group was necessary in order to determine the usefulness of the compounds proposed to be synthesized. Because of the greater reactivity of terminal acetylenes towards addition as compared with internal ethynes, our efforts, initially, were directed towards the preparation of the structurally simpler but synthetically more difficult monomers 1 and 2. If these more reactive acetylenes survived the initial condensation polymerization process, then the other non-terminal analogs would also be stable.

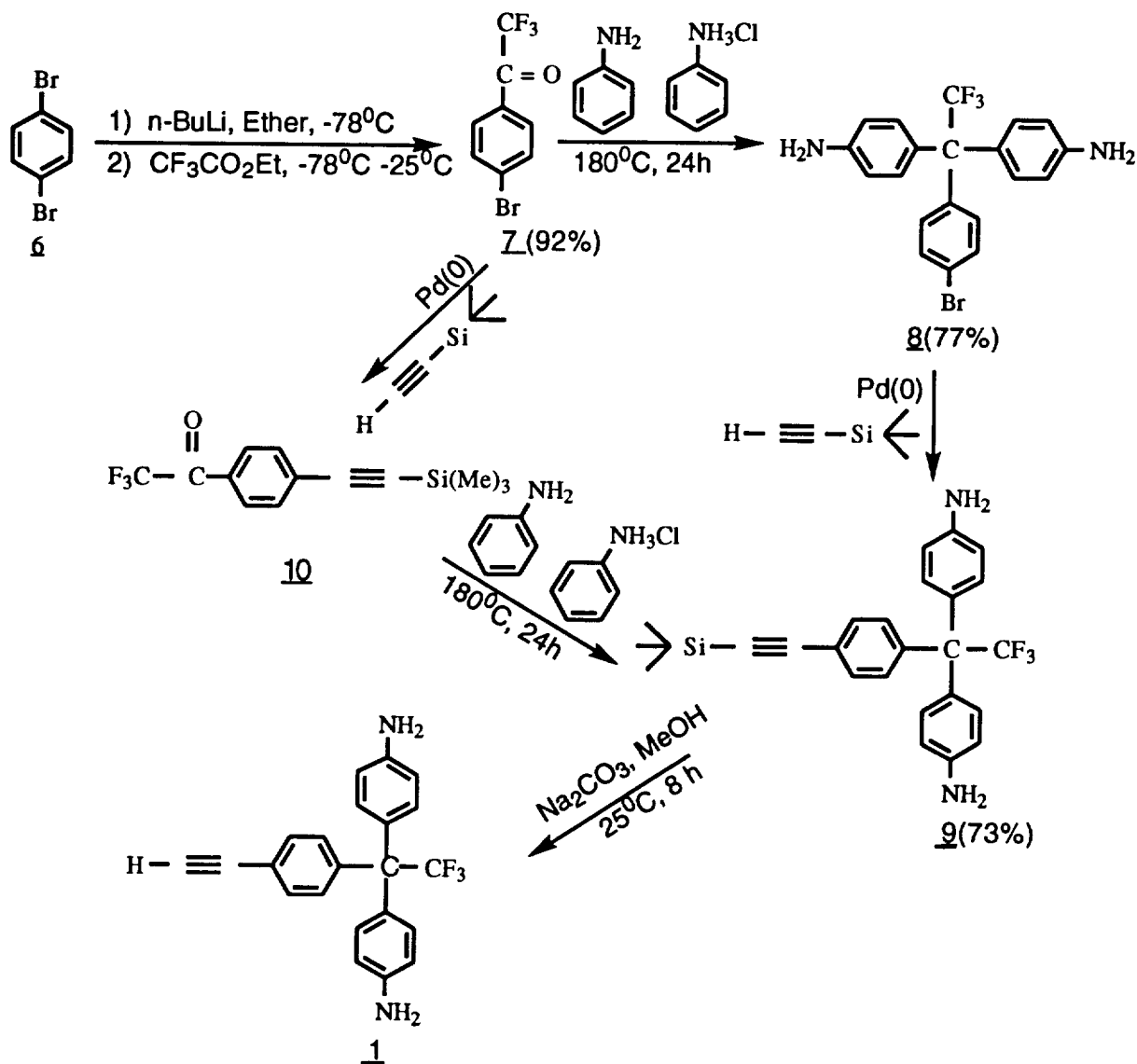
B.1.1. Synthesis of 1,1-Bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane

We have investigated the synthesis of 1 by two routes as shown in Scheme I, each of which began with the bromoketone 7. The yield of the bromoketone 7¹ was optimized to 92% in scaled-up reactions without having to use reverse addition technique.

One of the routes involves condensation of 7 with aniline by the method of Kray² to yield the diaminobromide 8 which would then undergo palladium(0)-catalyzed ethynylation with trimethylsilylacetylene (TMSA) to give the adduct 9. Deprotection of 9

would lead to the target compound 1.

Scheme 1



The diaminobromide 8 was obtained in 77% yield. Efforts to drive the $\text{Pd}(0)$ -catalyzed ethynylation of the diaminobromide 8 with TMSA to completion in triethylamine with less than 5 mol% of catalyst and CuI as co-catalyst were unsuccessful. Because all efforts to remove the unreacted diaminobromide from the coupled product proved futile, it was necessary to find a condition that would lead to

complete conversion of the bromide 8. This condition was found to be the use of a 3:1 vol/vol mixture of triethylamine and N-methylpyrrolidine. A yield of 73% of 9 was obtained by using this solvent mixture with 5 mol% each of Pd(0)-catalyst and CuI. Desilylation of crude 9 gave , in a scaled-up reaction, 79% of 1.

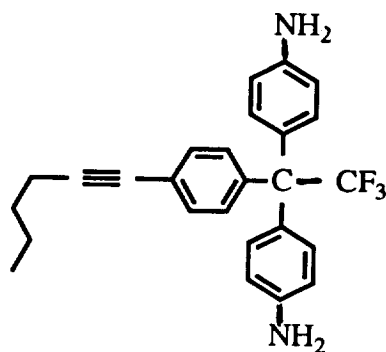
The alternative route to the monomer 1(see Scheme I) was undertaken to determine the optimal order for the two major reactions in the scheme - condensation and Pd(0)-catalyzed ethynylation. Pd(0)-catalyzed coupling of the bromoketone 7 was anticipated to be more facile than that of the diaminobromide 8 due to the activating effect of the carbonyl group. This was borne out by the fact that 7 was ethynylated completely with TMSA in triethylamine without the use of CuI as co-catalyst. Attempted Kray condensation of 10 with aniline gave a solid product which was not the expected 9(from ¹H NMR and mass spectrum).

After successfully developing and optimizing a synthetic scheme for the compound 1 , polymerization studies³ showed that the pendent ethynyl group could survive the conditions of polymerization. The resulting polymers also did cross-link on the curing of fabricated materials. With the usefulness of the ethynyl group for cross-linking of polymers formed by condensation reaction established, it was then certain that the other monomers projected for synthesis by us would be relevant to and useful in the studies to improve the properties of such engineering thermoplastics through ethynyl-based cross-linking.

B.1.2. Synthesis of Other Diaminotriarylethanes with Pendent Ethynyl Group(3 & 11).

The above optimized reaction condition for the ethynylation of 8 was applied to

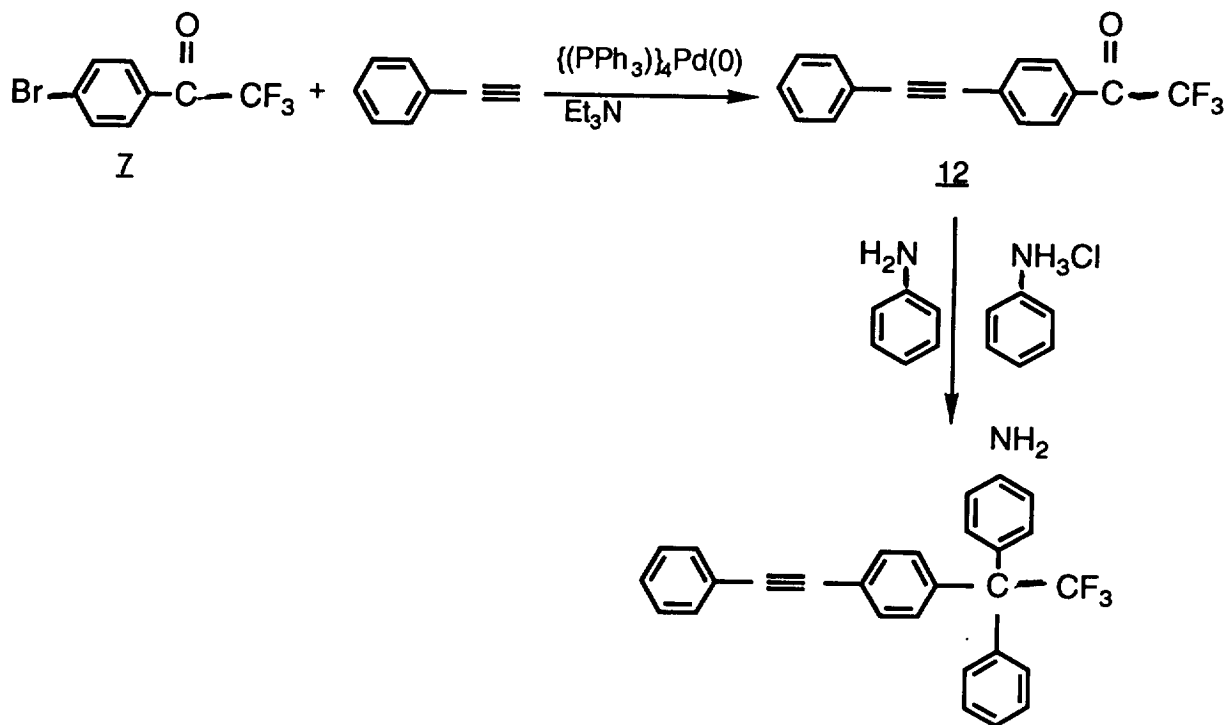
its coupling with phenylacetylene to give the monomer **3** in 61% and with 1-hexyne to give **11** in 76% yield. These additional acetylenes were used in order to investigate the effect of terminal substituents on the acetylene on the properties of resulting polymers.



11

The alternative route to the ethynylated monomers, which was not successful for the preparation of **1**, was however, successful with (phenylethynyl)-trifluoromethyl-acetophenone **12** (Scheme II).

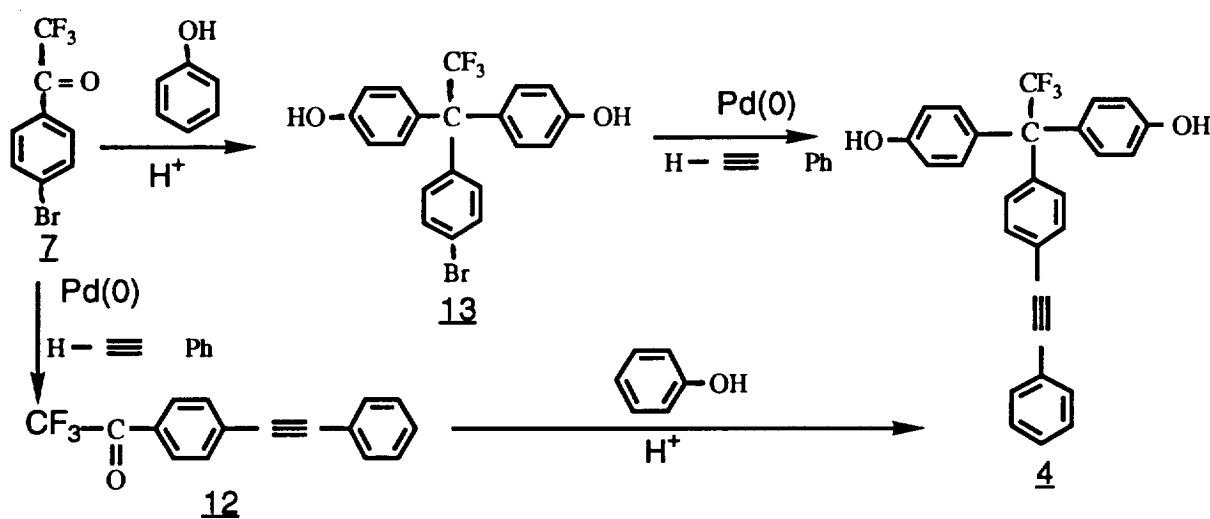
Scheme II



B.2. Synthesis of 1,1-Bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane 2
and Analogs 4 & 17.

For this class of monomers, we also examined two alternative routes, as illustrated in Scheme III with 4.

Scheme III

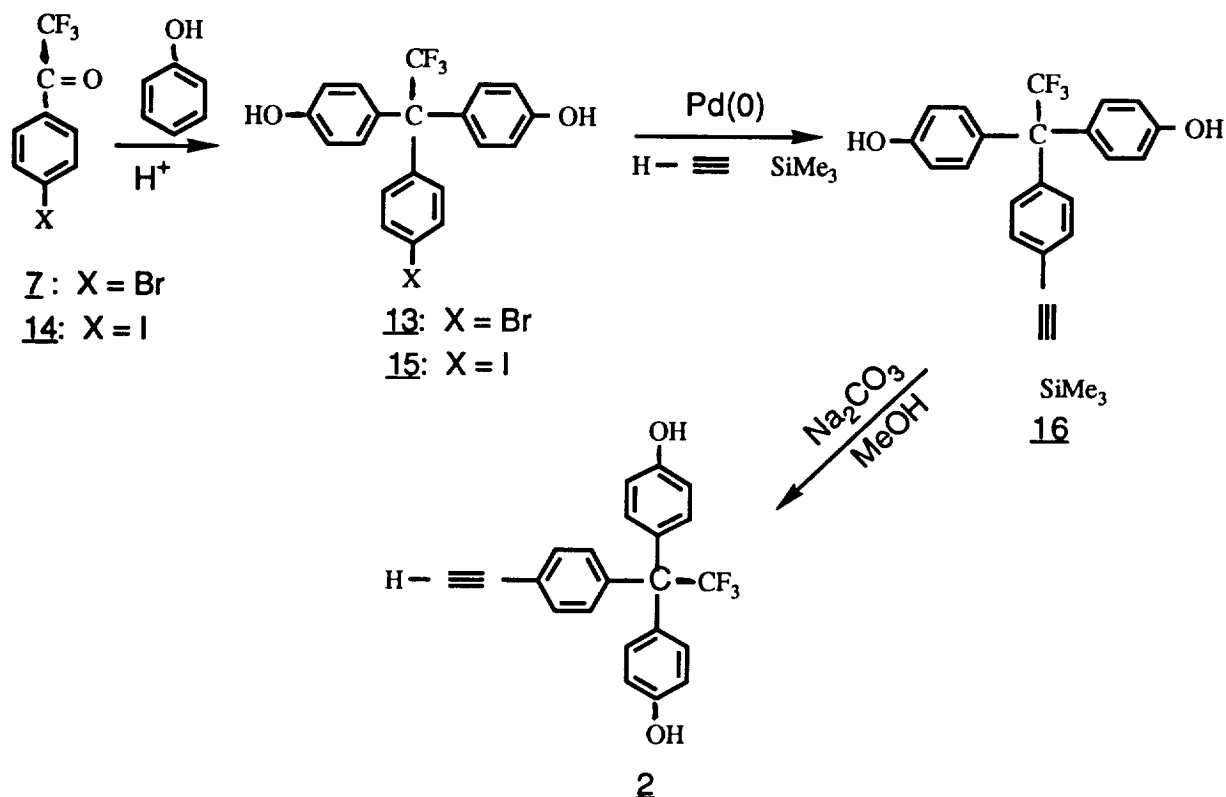


B.2.1 Synthesis of 1,1-Bis(4-hydroxyphenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane 2

The synthetic scheme for 2 is given in Scheme IV. Condensation of the bromoketone 7 with phenol using 2 - 6 mol% of triflic acid gave the bisphenol bromide 13 in 80% yield. With the iodoketone 14 the yield of the corresponding bisphenol iodide 15 was 77%. The bisphenol bromide was found to be more reactive than the diamino-analog as demonstrated by the fact that it's Pd(0)-catalyzed ethynylation with TMSA in triethylamine occurred with complete conversion of the bromide. The amount of Pd(0)-catalyst and Cul used was 4 mol% and the yield of the desilylated product 2

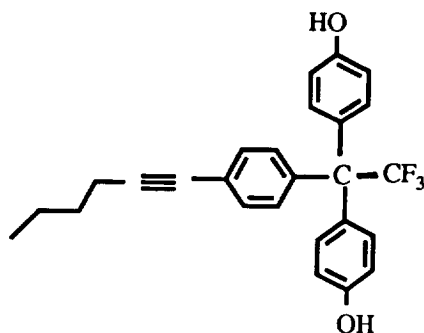
was 73%. The alternative route was not tried in the preparation of this compound.

Scheme IV



B.2.2 Synthesis of the Analogs 4 and 17:

The hexynyl coupling adduct **17** was prepared also in 73% yield by the same conditions used to prepare the trimethylsilyl adduct **16**. This condition and its other variations could not lead to complete conversion when the bromide **13** was coupled with phenylacetylene in attempts to prepare **4**. In order to overcome this difficulty, the iodide **15** was used instead. The Pd(0)-catalyzed coupling of the iodide **15** with phenylacetylene occurred with complete conversion of the iodide to give 82% of **4** using 4 mol% of Pd-catalyst and CuI in Et₃N.



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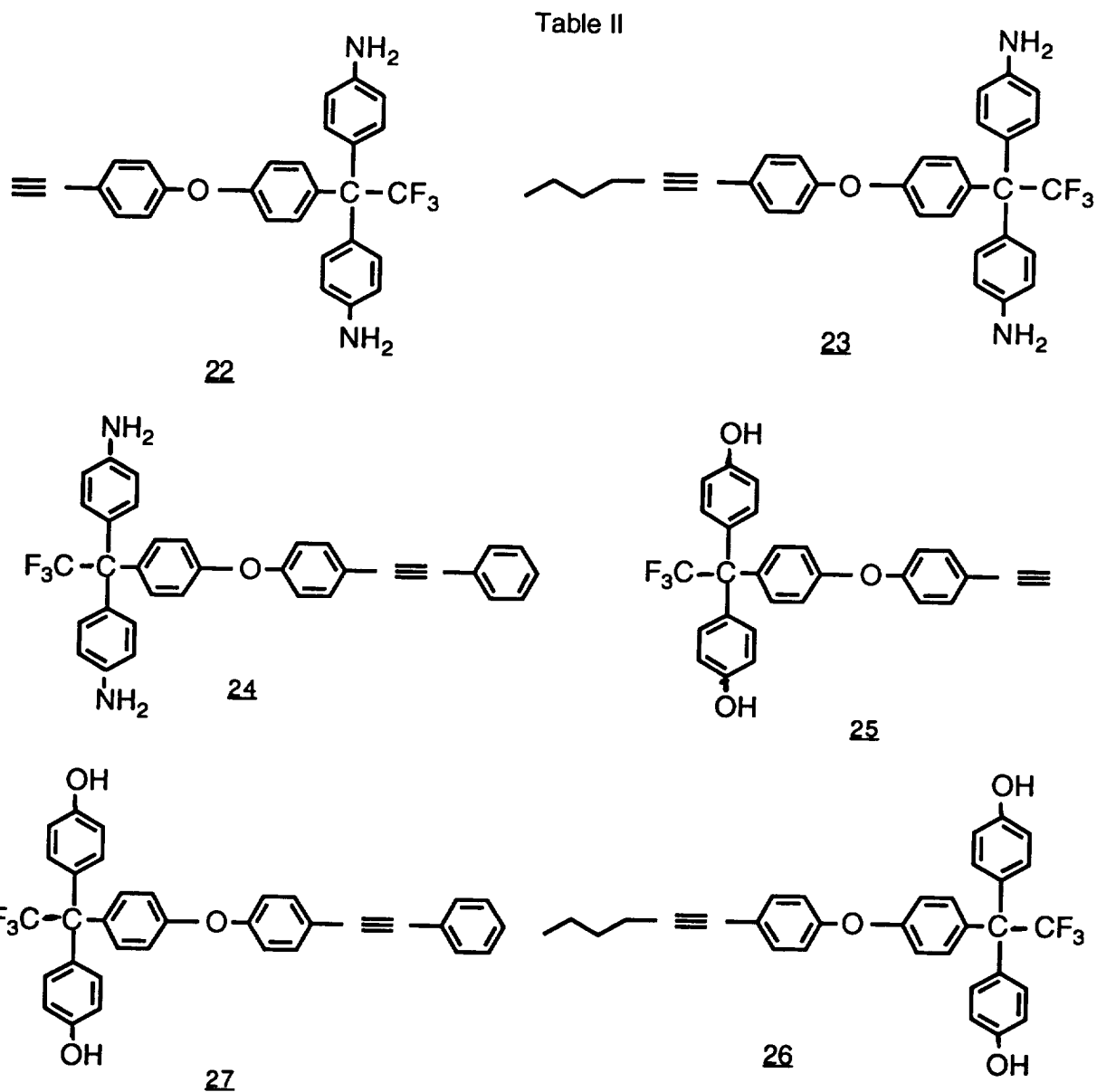
The alternative route involving ethynylation of the bromoketone Z followed by condensation with phenol was attempted with phenylacetylene as shown in Scheme V. Even though the condensation occurred at the carbonyl carbon, the initially formed product presumably suffered the addition of one and two molecules of phenol across the triple bond to give a mixture of two compounds. The exact structure of the multiple addition product has not yet been established.

B.3. Phenoxy Analogs of Triarylethanes with Pendent Ethynyl Groups

D.3. Difunctional 1,1-Diaryl-1-phenoxyphenylethanes With Pendent Ethynyl Groups:

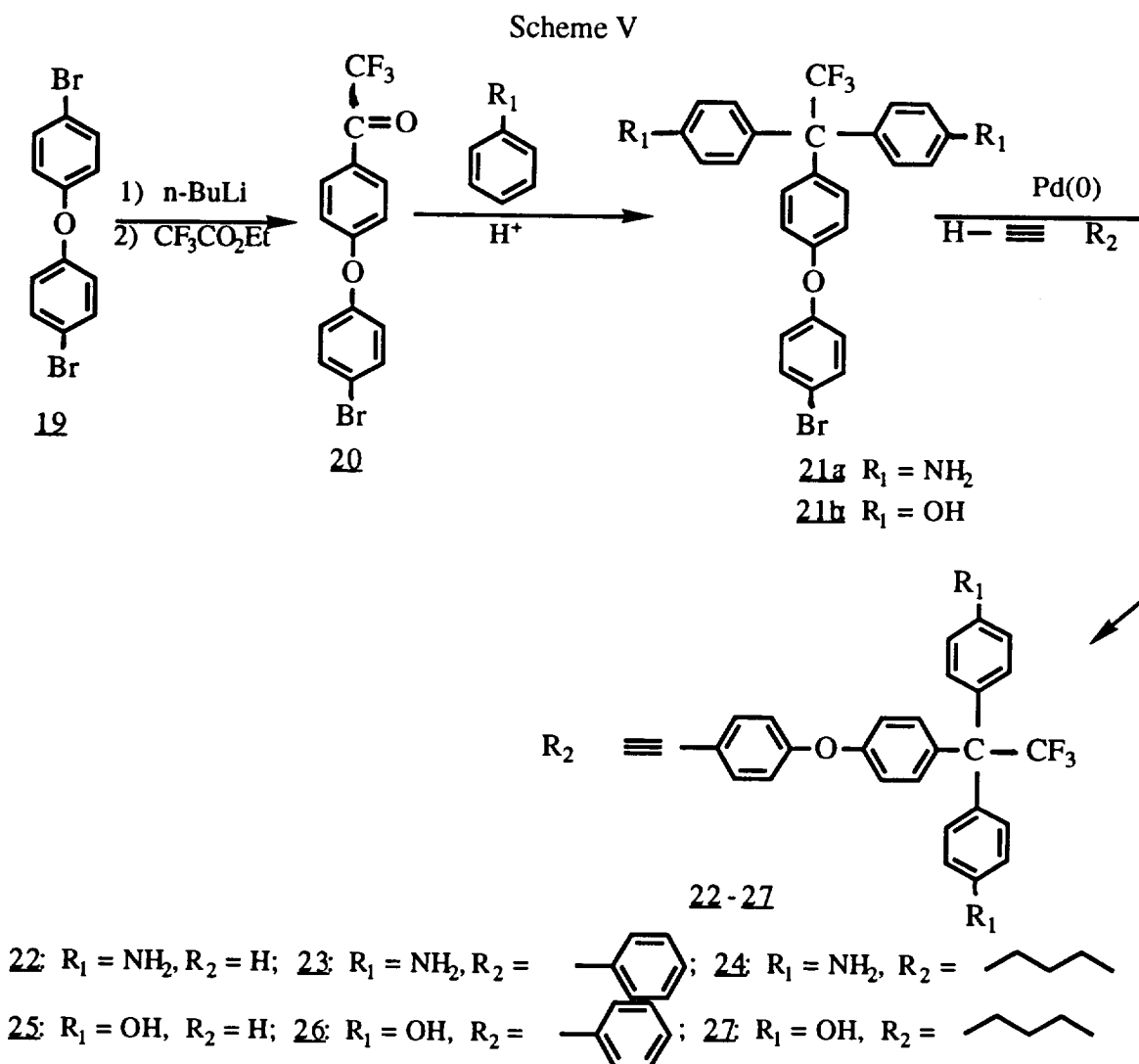
Compounds 22 - 27.

The synthesis of the diamino-compounds 22 - 24 and the bisphenols 25 - 27 (Table II) were developed from p-bromophenyl ether 19 according to Scheme V. In general, the ethynylation of 21 with all acetylenes was more sluggish in comparison with the analogous bromide Z. It was possible though to find conditions for exhaustive ethynylation. All six compounds were obtained in pure form and multi-gram samples submitted for polymerization studies.



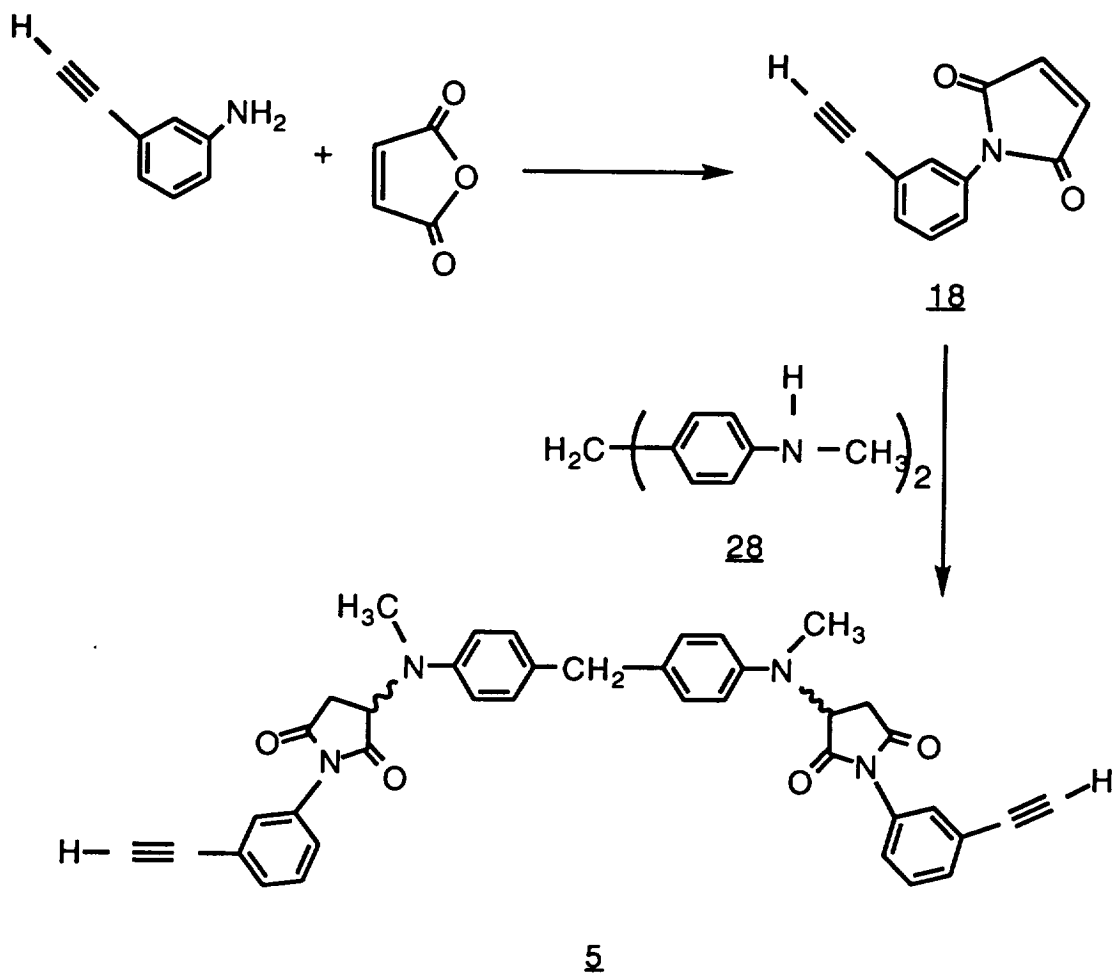
B.3. Acetylene-capped Tertiary Aspartimides

The preparation of samples of the tertiary aspartimide 5 followed a reported sequence for secondary acetylene-capped aspartimides⁴ as illustrated in Scheme VI. The maleimide 18 was obtained in 69% yield using N,N-dimethylformamide as



solvent. Attempted condensation of this maleimide with the diamine 28 in refluxing glacial acetic acid resulted in a discolored solid and a low mass balance for the reaction. Repeating the reaction at room temperature, however, resulted in a yellow suspension which was isolated by pouring in water. The mass balance for the reactions run this way varied from 91 - 100%. This material was identified to be 5.

Scheme VI



We have supplied from 10 - 20g of compounds 1, 2, 3, 4, 5, 11, 13, 17, 22 - 27 and 6g of 8 to our technical contact at NASA Langley Research Center for polymerization studies.

B.4. Personnel

This project, since the 1988/89 academic year, has supported the following two graduate students whose M.S. thesis research work were based on the project:

1. Ms. Miquel D. Antoine obtained her M.S. degree in the Spring of 1991 and joined the PhD program at Emory University, Atlanta. She later transferred to U. of Maryland, Baltimore County campus where she is about finishing her program.
2. Mr. Omari Ansong completed his M.S. degree requirements in the Spring of 1991. He is a resident alien. He worked Fall 1991, at the R & D Department of Hoechst Celanese in Providence, Rhode Island. He joined the polymer program at Rensselaer Polytechnic in Spring 1992.

Partial support was provided to the following graduate students:

3. Daniel Owusu graduated in 1990, worked for a year at NASA-LaRC and is currently in a PhD program at University of Pittsburgh.
4. Benjamin Ayida is currently writing his thesis.
5. Ms. Hilloah Reagh, a native american was supported during the summers of

1991 & 92. She later met graduation requirements by examination in 1994 and is currently working for Lab Force in Chesapeake.

6. An undergraduate junior, Mellanda Colson, was selected and received a scholarship in the form of tuition and stipend during the 1991-92 project year as part of our funding that year.

B.5. Professional Contributions

Results from this work have been presented in meetings and published in journals as listed below:

Synthesis of Difunctional Triarylethanes with Pendent Ethynyl Groups Monomers for Condensation Polymers. Ansong, O., Antoine, M. D., Nwokogu, G. C., Hergenrother, P. M., Accepted for publication in J. Org. Chem., 1994.

Poly(arylene ether)s With Pendent Ethynyl Groups, Jensen, B. J., Hergenrother, P. M., Nwokogu, G. C., J. Macromol. Sci-Pure & Appl. Chem., A30(6&7), 449, 1993; Polym. Prepr., 34(1), 1993

Polyimides with Pendent Ethynyl Groups. Jensen, B. J., Hergenrother, P. M., Nwokogu, G. C., Polym. Prepr., 33(1), 1992; Polymer, 43(3), 630, 1993.

CONTRIBUTED PAPERS:

The Synthesis of Ethynylated Difunctional Triarylethanes for High Performance Thermoplastics. Paper #404, 42nd Southeast/46th Southwest Combined Regional Meeting, ACS; New Orleans, Dec. 1990(with Miquel D. Antoine and Omari Ansong)

Synthesis of Bisphenolic Monomers for Cross-linkable Engineering Thermoplastics. 18th Annual Conference of The National Organization of Black Chemists and Chemical Engineers; Washington, DC, April 1991(with Omari Ansong)

Polyimides with Pendent Ethynyl Groups. ACS National Meeting, San Francisco, CA., April 1992; Polym. Prepr. 1992, 33(1), 914; with Jensen, B. J., and Hergenrother, P. M.

Poly(arylene ether)s with Pendent Ethynyl Groups. ACS National Meeting, Denver, CO; March 1993; Polym. Prepr. 1993, 34(1), 461; with Jensen, B. J., and Hergenrother, P. M.

Synthesis of Phenoxy Analogs of Difunctional Triarylethanes with Pendent Ethynyl Group. Nwokogu, G. C., 33rd National Organic Symposium, June 1993; Bozeman, Montana.

C. REFERENCES

1. Creary, X., *J. Org. Chem.*, **1987**, 52, 5026.
2. Kray, W. D., Rosser, R. W., *J. Org. Chem.*, 1977, 42, 1186.
3. All polymerization reactions and subsequent studies of the polymers were carried out by polymer scientists at langley Research Center.
4. Hergenrother, P. M., Havens, S. J., Connell, J. W., *Polym. Prepr.* 27(2), 408, **1986**.